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PHOSPHONIC ACIDS AND ESTERS XI[1]

A PHOTO-INDUCED ARBUZOV REARRANGEMENT OF TRIALKYL PHOSPHITES

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The cleavage of carbon-phosphorus bonds in triarylphosphines[2,3] and arylphosphonium salts[4] under photolytic conditions has been observed recently. For the trivalent compounds, photolysis in the presence of alcohols[2] or halide ions[3] leads to an effective disproportionation with the formation of tetra- and tri-valent products, i.e., tetraarylphosphonium salts and diarylphosphines. The primary process is postulated to be a homolytic cleavage of a carbon-phosphorus bond to produce aryl and diarylphosphinyl radicals. In an extension of these studies, we have found that a second class of trivalent organophosphorus compounds, trialkyl phosphites, undergo a related photolytic reaction leading to tetravalent products.

The photolysis of degassed trimethyl phosphite (Ia) was carried out at 20° for 48 hours under nitrogen in the absence of solvent employing a 450 watt Hanovia lamp in a quartz immersion well. Examination of the infrared and PMR spectra of the reaction mixture indicated the development of phosphonyl and methyl-phosphorus groupings. GLC analysis of the reaction mixture showed the presence of unreacted Ia, dimethyl methylphosphonate (IIa, 32.6%), dimethyl phosphite (IIIa, 3.1%) and trimethyl phosphate (IVa, 12.3%). In addition to these products, a significant amount of Ia was converted to higher molecular weight products (11.0% based on isolation exper-

$$\underset{\text{I}}{(RO)_3P:} \xrightarrow{h\nu} \underset{\text{II}}{RP(O)(OR)_2} + \underset{\text{III}}{(RO)_2P(O)H} + \underset{\text{IV}}{(RO)_3PO}$$

a, R = CH_3; b, R = C_2H_5; c, R = i-C_3H_7; d, R = n-C_4H_9

iments). The mass spectrum of the reaction mixture showed peaks with M/e values characteristic of IIa and IVa, IIIa and a material with parent mass 232. The latter material was identified as tetramethyl methylenebisphosphonate [$(CH_3O)_2P(O)CH_2P(O)(OCH_3)_2$, V] by a comparison of mass spectral fragmentation patterns with those of an authentic sample. Additionally, a small amount (<4%) of gaseous products (92.8% methane, 7.2% ethane) was formed during photolysis.

The photolyses of triethyl (Ib), tri-i-propyl (Ic) and tri-n-butyl (Id) phosphites under identical conditions led to similar results. In each case, the dialkyl alkylphosphonate (II) was the major photolysis product. The observed results are summarized below.

Trialkyl Phosphite Photolyses

Reaction Mixture Composition (% by GLC Analysis)

R =	CH_3 (a)	C_2H_5 (b)	i-C_3H_7 (c)	n-C_4H_9 (d)
$(RO)_3P$ (I)	49.0	61.4	38.1	46.2
$RP(O)(OR)_2$ (II)	32.6 (64.0)*	22.4 (58.0)*	20.5 (33.2)*	38.6 (71.9)*
$(RO)_2P(O)H$ (III)	3.1	8.0	10.5	2.3
$(RO)_3PO$ (IV)	12.3	8.3	10.0	10.5
Volatiles	<4.0	<3.0**	trace	trace

*% Conversion of I to II, based on unrecovered I.

**91.2% C_2H_6, 8.7% CH_4, 2.1% C_4H_{10}.

The mass spectra of reaction mixtures from the photolyses of Ib, Ic and Id indicated the presence of a highly complex mixture of high molecular weight materials (M/e values to a maximum of 395 for Id).

The observed predominance of the dialkyl alkylphosphonate (II) in the photolysis products indicates that this reaction is effectively an example of photoinitiation of the Arbuzov rearrangement. The Arbuzov reaction, the isomerization of I to II, has been shown to be initiated by the attack of both ionic and free radical agents on I.[5] Although these studies do not allow any assignment of mechanism for the photoinitiated formation of II, feasible mechanisms based upon either initial photoexcitation of I to a triplet state or initial homolysis of a carbon-oxygen bond in I may be envisioned. The observed amounts of trialkyl phosphates (IV) formed in the reaction are greater than can be accounted for on the basis of simple photooxidation[6] and their formation can most probably be attributed to the attack of photolytically generated alkoxyl radicals on I.[7] The detection of alkanes as minor reaction products is consistent with this interpretation.

The isolation of V in the photolysis of Ia indicated that the initially formed phosphonate IIa was probably undergoing photolytic decomposition. Attack of a photolytically generated $\cdot CH_2P(O)(OCH_3)_2$ radical on Ia would constitute a plausible course for the formation of V. In order to investigate this possibility, IIa was photolyzed under the previously described conditions. PMR analysis indicated a 17.5% decomposition of IIa; carbon dioxide, methane, ethane and propane were isolated. The mass spectrum of photolyzed IIa indicated a complex mixture with peaks of M/e to a maximum of 262; V was not present in the reaction mixture. GLC analysis indicated IIa to be essentially the only low molecular weight phosphorus containing material in the photolysis mixture.

The photoinitiated Arbuzov rearrangements examined in this study are considerably slower than other recently reported photochemical processes involving I as substrates. Both the photooxidation[6] and photoinitiated arylation[8] of I proceed at sufficiently high rates so that the photoinitiated conversion of I to II is not generally observed as a competing process.

In an attempted extension of the reaction, the photolysis of certain phenylated derivatives of trivalent phosphorus (triphenyl phosphite, diethyl phenylphosphonite, ethyl diphenylphosphinite) were investigated. In each case, the starting material was completely unchanged after a photolysis period of 48 hours.

Further studies directed toward an elucidation of the mechanism of this reaction and its synthetic application for the formation of novel phosphonates are in progress. We are indebted to the Mellon Institute for providing facilities for this research; this study was supported in part by the Directorate of Chemical Sciences, Air Force Office of Scientific Research under Grant No. AF-AFOSR-470-64.

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